

## Civil & Environmental Engineering Graduate Student Theses & Projects

### Environmental

- Andria Costello
- Charles Driscoll
- Chris Johnson
- Ray Letterman

### Geotechnical

- Shobha Bhatia
- Samuel Clemence
- Dawit Negussey

### Structural

- Riyadh Aboutaha
- Eric Lui

### Dr. Andria Costello's Students

**Mahendra, Shaily -- MS in Environmental Engineering, August 2001**  
***Effects of Trace Metals on Bioremediation by Methanotrophs***

#### Abstract

Methane oxidizing bacteria can be used as microbial remediation systems because they can cometabolize several hazardous organic compounds, such as trichloroethylene (TCE), using the methane monooxygenase (MMO). In contaminated sites where TCE and other solvents exist along with trace metals,, these metals have the potential to influence the growth of in-situ methanotrophs, expression of the MMO and rates of biotransformation reactions. In this study, the effects of copper, nickel and zinc were investigated on the growth of *Methylosinus trichosporium OB3b*, which can express both the soluble and the particulate forms of MMO,, and *Methylocystis parvus OBBp*, which expresses particulate MMO only. Additionally, the effects of metals on the degradation of TCE by these methanotrophs were examined.

The speciation of copper, nickel and zinc in NMS medium was determined by chemical equilibrium modeling. Soluble metal-EDTA complexes were preferentially formed, followed by equilibrium between free ions and other dissolved and precipitated compounds. In mixtures, nickel and zinc influenced the concentrations of free  $\text{Cu}^{2+}$  ions. In whole cell experiments, the growth rates of both methanotrophs tested decreased with increase in copper and nickel

concentrations. For OBBp grown in different concentrations of zinc, the growth rate decreased with increase in zinc concentrations up to 400  $\mu\text{M}$  zinc. For OB3b, the growth rates decreased with increasing concentrations of zinc. In TCE degradation experiments using 20  $\mu\text{M}$  TCE, degradation by both methanotrophs followed the trends observed for growth in the presence of NMS medium containing added metals. The highest rates of TCE degradation were observed by *Methylosinus trichosporium OB3b* expressing sMMO in the medium containing no added metal.

These results suggest that metals in the environment will affect on the growth of methanotrophs and biodegradation of trichloroethylene but these effects will be different on different methanotrophs. The data presented here will be useful as an initial step towards predicting the rate and extent of natural or enhanced bioremediation carried out by methane bacteria in the presence of various contaminating metals.

**Todorova, Svetoslava – MS in Environmental Engineering, December 2003**  
***Iron geochemistry and microbial diversity of iron-reducing microorganisms in a minerotrophic wetland***

Abstract

This study investigated the geochemistry and microbial diversity associated with iron reduction at a minerotrophic wetland in central New York state. Fine-scale investigations of the peat and peat porewater were carried out to allow detailed vertical analyses of iron chemistry. Results revealed that Fe(II) was produced in situ in the wetland, most probably as a result of microbial Fe(III) reduction. Fe(II) concentration profiles suggested existence of Fe(III) reduction in the zone adjacent to the agricultural field, while no significant evidence for Fe(III) reduction existed in the pristine zone. The microbiological study did not confirm the observed geochemical contrast between zone I and zone II. Results revealed that iron-reducing members of the genus *Shewanella* were present in both zones. Theoretical equilibrium modeling based on geochemical indicators predicted that the difference in soluble iron concentrations could be a result of abiotic reactions, such as pyrite precipitation. Microbiological results supported that hypotheses. Geochemically, a correlation between Fe(II) and bulk density proved the importance of iron reduction in the decomposition of organic matter in the organic rich peat and demonstrated the importance of the mineralogical composition on the reduction of Fe(III). A unique reversion of iron and sulfate reduction in the zone adjacent to the agricultural field, along with comparative analysis of other studies, revealed an interesting trend in minerotrophic wetlands.

**Schneider, Erin-Rose – MS in Environmental Engineering, December 2003**

***The effects of soil chemistry on the diversity and function of natural methanotroph populations***

Abstract

Acidity levels in atmospheric deposition vary over the Adirondack Mountain Region of New York, decreasing from west to east. The objective of this study was to determine if the pH of the soils changed the phylogenetic position of methane oxidizing bacteria found in the soils of this region, their methane oxidation potentials, and/or their numerical abundance. The 16S rRNA genes from natural populations of methaneoxidizing bacteria were polymerase chain reaction (PCR) amplified from total community DNA extracted from acidic forest soils from two sites within the Adirondack Mountains. The two sites were Sunday Lake watershed, located on the western edge of the Adirondack park, and Huntington Forest, located near the geographic center of the Adirondack park. It was determined that these environmental gene sequences were most phylogenetically similar to those from acidophilic methanotrophs isolated from acidic peat bogs. However, there seemed to be no difference between the diversity of the communities at the two Adirondack sites. The methane fluxes were measured at the same two sites. Both sites showed an average net influx of methane, although the measured flux at Sunday Lake watershed was more comparable to fluxes measured in other forested sites. The methane fluxes at both Sunday Lake watershed and Huntington Forest were poorly correlated with soil pH. The abundance of both type I and type II methanotrophs was determined by fluorescence in-situ hybridization. Type I methanotrophs were observed to outnumber type II methanotrophs by approximately 3% in the total bacterial population. Type I methanotrophs at Sunday Lake watershed also showed a negative correlation to soil pH ( $r^2 = 0.676$ ,  $p = 0.05$ )

**Bremer, Mark – MS in Environmental Engineering, December 2004**

***Indicators of acid stress in northeastern forest soil methane oxidizing communities***

Abstract

Acidification of forest ecosystems due to acid deposition has been shown to decrease acid neutralizing capacity (ANC) and adversely affect microbial community structure, function, and diversity. In this study, I describe the effects of acidification on soil methane oxidizing communities in the Northeastern United States and provides evidence of changing chemical and biological indicators of acid stress in forested headwater catchments. Biological methane oxidation in soils is an important global sink of methane, a potent greenhouse gas, and can contribute up to 15% of total methane consumption annually. Methane oxidation rates are sensitive to changes in pH, but the effects of acid deposition on natural methane oxidizing communities are unknown.

Reduced strong acid inputs have not been accompanied by increases in ANC as expected, and many remote forest soils and streams remain chronically acidic. Stream water chemistry was investigated to determine what is suppressing the ANC and contributing to acidification of streams. Naturally occurring organic acids, measured with dissolved organic carbon (DOC), showed significant relationships when regressed against ANC.

*In situ* hybridization (FISH) with rRNA-targeted, fluorescently labeled oligonucleotide probes was used with confocal scanning laser microscopy to enumerate and compare methanotrophic bacteria in forest soils affected by varying amounts of atmospheric acid deposition. Surface soil horizons showed relatively low numbers of methanotrophs in all seasons, but organic and mineral horizons varied widely. Type II methanotrophs showed a moderate correlation with soil pH.

Terminal restriction fragment (TRF) analysis was conducted on environmental 16S rRNA gene samples to determine fingerprints of microbial methane oxidizing communities. Inherent differences exist between the tested methanotroph communities and known strains of methanotrophs. Samples exposed to higher levels of acid deposition did not show lower numbers of methane oxidizers, but suggested a shift in community structure to favor unknown acid tolerant species.

## **Dr. Charles Driscoll's Students**

### **Chen, Limin -- MS in Environmental Engineering, 2001**

***The application of an integrated biogeochemical model (PnET-BGC) to lake/watershed ecosystems in the Adirondack and Catskill regions of New York***

#### Abstract

The Adirondack and Catskill regions of New York are characterized by high rates of acidic deposition and large numbers of acidic surface waters (acid neutralizing capacity; ANC <0  $\mu\text{eq/l}$ ). Despite high inputs of acidic deposition, there is considerable variability in acid-base status of surface waters in the Adirondacks and Catskills. In this study, the response of different forest and aquatic ecosystems in these two regions to changes in atmospheric deposition was investigated using an integrated forest-soil-water model PnET-BGC. The model was applied to several representative sites in the Adirondacks and Catskills. These sites include an acid sensitive watershed (Constable Pond; ANC  $\approx$ -8 $\mu\text{eq/l}$ ), a relatively insensitive watershed (Arbutus Pond; ANC $\approx$ 67 $\mu\text{eq/l}$ ), a dystrophic lake/watershed (West Pond; DOC $\approx$ 630 $\mu\text{molC/l}$ , ANC=2 $\mu\text{eq/l}$ ) and a watershed with mature forest (Willy's Pond, ANC=-10 $\mu\text{eq/l}$ ) in the Adirondacks and an acid-sensitive watershed in the Catskills (Biscuit Brook, ANC=20 $\mu\text{eq/l}$ ). Results of simulations showed that the model predicted annual volume-weighted concentrations of the major constituents of surface waters, pH and ANC agreed reasonably well with measured data and generally captured the long-term trends. The model simulated element fluxes and pools compared well with measurements

from other studies. Acid neutralizing capacity budgets were developed based on the fluxes simulated by PnET-BGC for each site. Model simulations also showed over the long term, atmospheric deposition has altered the soil and surface water chemistry. Moreover, response of these watersheds to ongoing and potential future sulfur dioxide and nitrogen oxide emissions control programs were also investigated. Model simulations indicate even with the controls specified in the 1990 CAAA (Clean Air Act Amendment), the sensitive sites in Adirondacks and Catskill area will continue to experience chemical conditions adverse to forest growth and aquatic biota. Additional decreases in strong acid inputs significantly improve the chemical conditions and accelerate recovery rates in surface water ANC.

**Lindeman, Margaret -- MS in Environmental Engineering, 2001**

***The cycling and fate of mercury in the Sunday Lake watershed, Adirondack region of New York***

Abstract

The Sunday Lake watershed, located in the Adirondack region of New York, was studied in order to develop a mercury (Hg) mass balance for the lake and watershed ecosystems. Analysis was conducted on surface water, soil, soil water, and sediment to determine the concentrations and fluxes of total Hg ( $Hg_r$ ) and methyl Hg ( $CH_3Hg^+$ ) in compartments of the watershed. Samples were also analyzed for major anions, major cations, dissolved organic carbon (DOC), pH, acid neutralizing capacity (ANC) and aluminum for interpretation of Hg data and future use in model development. A program was established with the Mercury Deposition Network (MDN) at Huntington Forest (approximately 75 km from Sunday Lake), to analyze precipitation samples for  $Hg_r$  and  $CH_3Hg^+$  concentrations. The wet deposition of  $Hg_r$  and  $CH_3Hg^+$  were estimated to be  $10.9 \mu g / m^2 - yr$  and  $0.06 \mu g / m^2 - yr$ , respectively. Soil concentrations of  $Hg_r$  were highest in the forest floor (13-189 ng/g dry weight). Soil concentrations were low in the E horizon (3.9-25.2 ng/g), higher in the zone of organic deposition in the mineral soil (Bh horizon; 3.7-67.5 ng/g) and low in the lower mineral soil or Bs horizon (2.7-47.5 ng/g). The mean  $Hg_r$  concentrations in the Oa, E, Bh, and Bs1 and Bs2 soil horizons were 77.2 ng/g, 8.49 ng/g, 30.2 ng/g, 20.6 ng/g, and 21.9 ng/g, respectively. Concentrations and fluxes of  $Hg_r$  in soil solution were highest in the Oa horizon (forest floor leachate), and lower in the Bh and Bs horizons (mineral soil leachate). The mean soil solution  $Hg_r$  concentrations in the Oa, Bh and Bs horizons were 22.4 ng/L, 8.39 ng/L, and 3.46 ng/L, respectively, and the mean  $CH_3Hg^+$  concentrations were 0.11 ng/L, 0.44 ng/L, and not detected ( $<0.04$  ng/L), respectively. The fluxes of  $Hg_r$  through the Oa, Bh, and Bs horizons were estimated to be  $26.4 \mu g / m^2 - yr$ ,  $9.26 \mu g / m^2 - yr$ , and  $2.02 \mu g / m^2 - yr$ , respectively. The  $CH_3Hg^+$  fluxes through the Oa, Bh, and Bs horizons were estimated to be  $0.13 \mu g / m^2 - yr$ ,  $0.3 \mu g / m^2 - yr$ , and  $0.012 \mu g / m^2 - yr$ , respectively. The elevated flux of  $Hg_r$  draining the forest floor may be due to dry deposition or a net release of  $Hg_r$  from the forest floor due to elevated atmospheric deposition of  $Hg_r$  in the recent past. Mercury and DOC concentrations in soil water were strongly

correlated ( $r^2=0.81$ ). Lake inlet concentrations of  $Hg_r$  ranged from 0.8 ng/L to 12 ng/L, with a mean concentration of 3.1 ng/L. Methyl Hg concentrations were lower, ranging from less than 10% to over 50% of  $Hg_r$ . Lake water concentrations of  $Hg_r$  ranged from 2.0 ng/L to 4.6 ng/L, and  $CH_3Hg^+$  concentrations ranged from non-detectable values ( $<0.04$  ng/L) to 2.5 ng/L. A mass balance showed that 79% of wet Hg deposition was retained in the watershed and 15% of  $Hg_r$  was retained in Sunday Lake. Mass balance calculations also showed that the watershed and the lake were sources of  $CH_3Hg^+$ . Sediment deposition of Hg has increased 2.7 - fold since 1900. In recent years, this rate has decreased 32% from the peak rate, which occurred around 1978.

**Lorey, Peter -- Ph.D. in Chemistry, 2001**

***The determination of ultra trace levels of mercury in environmental samples in the northeastern United States: Inferring the past, present, and future of atmospheric mercury deposition (New York, New Hampshire, Vermont)***

Abstract

The interest in mercury (Hg) contamination lies primarily in the fact that fish containing high levels of Hg are a part of the human diet. However, the reactions and pathways of Hg before it is assimilated into fish tissue are complex, and in some cases still not well understood. Although Hg is naturally occurring, the concentrations that are measured today, from historical records such as sediment cores and ice cores, are higher than those in preindustrial times. This leads to the conclusion that anthropogenic activities have caused these increases, even in remote areas. In this study the concentrations of total mercury (HgT) were measured in sediment cores from eight lakes in the Adirondack region of New York. Using the results, historical profiles were created for each lake showing the change in flux of HgT to the sediments over the past 200 years. An increase of 3.5 times above preindustrial values was found, but there has been an evident decline in recent years. The watershed of the lakes was important in the accumulation of Hg in lake sediments. Another portion of this study involved the analysis of Hg concentrations in water and sediment from 94 lakes in Vermont and New Hampshire. Relationships were developed with physical and chemical data from the lakes in order to elucidate some of the factors that influence the Hg concentrations in lakes in this region. The Hg concentrations were found to be most strongly related to the mean depth, residence time, and pH, and the concentrations of dissolved organic carbon, chloride, and dissolved oxygen of the lakes. The biggest influence of the watershed land use on Hg concentrations was its affect on the chemical characteristics of the lake. Atmospheric emissions of Hg will be coming under more strict regulations in the forthcoming years. In order to implement regulations with the maximum effectiveness and still be cost effective, a better understanding of Hg behavior is imperative. With an ultimate goal of reducing human health risks from Hg contaminated fish, these results are another step towards shaping the future of atmospheric Hg deposition and its consequences.

**Wellington, Brian -- PhD in Civil Engineering, 2002**

***Controls on dissolved organic carbon at Hubbard Brook Experimental Forest and its effects on stream acid-base chemistry***

Abstract

In this study, I investigated the factors that control the spatial and temporal variations in stream and soil solution dissolved organic carbon (DOC) concentrations and composition within a north-facing watershed (Watershed 9) and across the forested valley at the Hubbard Brook Experimental Forest, New Hampshire. Soil solutions displayed horizontal patterns in DOC fractions with hydrophobic acids dominating in the Oa horizon. Hydrophobic acids were also the dominant fraction in stream water DOC. Temporal variations in the proportion of DOC fractions were mainly evident in the Oa soil horizon leachate and stream water. Stream DOC fractions varied spatially, with increases in the concentration of both hydrophobic and hydrophilic acid fractions with increasing elevation, however hydrophobic acids increased more markedly. Various factors were related to spatial variations in stream DOC concentration and composition including variations in forest floor C, topographic index, soil depth, and slope. However, forest floor C concentrations exhibited the strongest relationship. During hydrologic events, hydrophobic acids dominated DOC increases at peak discharge. During both base flow and at peak discharge during events, the ratio of hydrophobic acids to hydrophilic acids suggested that DOC in the stream largely originated from a wetland at the headwaters of Watershed 9. Organic acids are generally thought to play a minor role in the episodic acidification of streams in the U.S., mainly because most streams studied to date are characterized by low concentrations of DOC. I hypothesized that in streams with high concentrations of DOC, episodic acidification will be controlled by increases in naturally occurring organic acids. During snow melt events, organic acids were a minor contributor to the short-term acidification of stream water, with increases in NO<sub>3</sub><sup>-</sup> and dilution of base cations being the dominant mechanisms. During summer rainfall events however, increases in inputs of organic acids were the dominant mechanism of episodic acidification when soil water was the dominant contributor to stream discharge. Also precipitation events occurring after relatively wet antecedent conditions were likely to result in more severe acid episodes than events that followed drier antecedent conditions.

**Geary, Robert -- PhD in Civil Engineering, 2003**

***The role of aluminum in regulating the retention of cations and dissolved organic carbon in organic forest soil horizons***

Abstract

Processes in organic forest soil horizons can play an important role in influencing surface water quality especially in watersheds where shallow flow paths through soil are important. Aluminum has an extremely high affinity for the acidic functional groups present in soil organic matter and binds nearly irreversibly with these groups. This reaction alters the response of organic forest soil horizons to

atmospheric deposition as well as other environmental conditions such as calcite treatment. In this study, I evaluated the effect of organically bound aluminum on the retention of cations and dissolved organic carbon (DOC) in organic forest soil horizons. Field and laboratory results were consistent with the reaction of aluminum with acidic functionality present in soil organic matter, and the resultant effect this reaction has on specific and nonspecific binding of protons and cations, and on DOC release. Under acidic conditions, increasing bound aluminum in organic forest soil horizons was shown to: (1) decrease acidity, and calcium concentrations in soil and solution; (2) decrease release of DOC from soil; and (3) increase aluminum concentration in soil solution. Bound aluminum had similar, but less influence under alkaline conditions, especially with respect to calcium concentrations in soil and solution. Results also showed that the heterogeneity of soil organic matter can diminish the strength of relationship observed between bound aluminum, and other solid and solution phase constituents present in organic forest soil horizons. Field and laboratory results were reproducible with the Windermere Humic Aqueous Model (WHAM); a mechanistic model that describes proton and metal binding to humic and fulvic acids, and the effect of this binding on the solubility of organic matter. Simulations using WHAM showed that bound aluminum increased the response of organic forest soil horizons and associated solution to the environmental conditions evaluated in this study (i.e., calcite treatment of 9 Mg/hectare and a 50% reduction of individual and combined loading of basic cations and mineral acid anions). Simulations predicted that organic forest soil horizons with higher bound aluminum content would typically respond faster, and produce soil solutions with higher aluminum, and lower hydrogen ion, calcium and DOC concentrations than organic forest soil horizons with lower bound aluminum content.

**Kalicin, Melissa -- MS in Environmental Engineering, 2003**  
***Cycling of mercury in an Adirondack terrestrial ecosystem***

Abstract

The dynamics of mercury were studied at Sunday Lake Watershed (SLW) in the Adirondack region of New York State. This study focused on two forest plots with coniferous and deciduous vegetation. These plots were investigated for the dynamics of total mercury ( $Hg_T$ ) and methyl mercury (MeHg) in precipitation, throughfall, leaf litter, soil, and soil water. Precipitation  $Hg_T$  flux at SLW was approximately  $9 \mu g/m^2$ -yr. Higher concentrations of  $Hg_T$  occurred in throughfall at the coniferous site (3.0-38.2 ng/L, mean 23.7 ng/L  $Hg_T$ ) than at the deciduous plot (1.0-3.8 ng/L, mean 2.0 ng/L  $Hg_T$ ). Leaf litter concentrations of  $Hg_T$  differed among individual tree species but not significantly among plots (coniferous mean  $58 \pm 18.4$  ng/g, deciduous mean  $50.6 \pm 11.6$  ng/g). However, MeHg concentrations were greater in the leaf litter at the deciduous plot (mean  $8.4 \pm 4.6$  ng/g) than at the coniferous plot (mean  $0.64 \pm 0.54$  ng/g). The flux of mercury to the forest ecosystem was dominated by dry deposition (throughfall and litter fall). However, the pathway of mercury inputs differed among plots;  $Hg_T$  fluxes via throughfall and litter were 32 and  $6 \mu g/m^2$ -yr, respectively, at the coniferous plot and 7 and  $15 \mu g/m^2$ -yr, respectively, at the deciduous plot. Total mercury concentrations in soil

varied with horizon but not significantly among plots. Soil  $Hg_T$  concentrations were greatest in the Oa horizons (13.2-188.9 ng/g), lowest in the E horizons (3.9-25.2 ng/g), exhibited a peak in the Bh horizons (3.7-67.5 ng/g) and values decreased in the Bs horizons (2.7-47.5 ng/g). Soil concentrations of  $Hg_T$  were strongly correlated with concentrations of soil organic carbon. Concentrations of  $Hg_T$  in the soil solutions were highest in the forest floor leachate (9.8-41.8 ng/L) and decreased in the soil solution concentrations through the Bh horizon (0.9-13.9 ng/L) and in the Bs horizon (0.9-11.0 ng/L) at both sites. Methyl mercury concentrations in the soil were relatively uniform throughout both forest soil profiles (1.0-2.2 ng/L) whereas, soil solutions were highly variable (below detection limit ( $\leq 0.02$ )-1.4 ng/L) and similar among plots. Mass balance calculations show that the soil was a net sink for inputs of  $Hg_T$  and MeHg at both the coniferous and deciduous plots.

**McLaughlin, Erin -- MS in Biology, 2003**

***Mercury dynamics in a lake/watershed ecosystem : vegetation patterns and aquatic trophic transfer***

#### Abstract

High mercury (Hg) concentrations have been reported in fish collected from remote lakes, including lakes within the Adirondack Park, New York. Mercury is a known neurotoxin and fish serve as the primary source of Hg for humans. This study was part of a whole-watershed project designed to improve understanding of Hg cycling within an Adirondack watershed and how it influences fish Hg concentrations.

This study was conducted in two phases. The first phase examined the role of vegetation in the cycling of Hg within the Sunday Lake watershed. Mercury concentrations in upland and riparian wetland vegetation were studied over a growing season. Vegetation concentrations were generally within the range of literature values. No significant differences were found between sun and shade foliage. *Sphagnum spp.* total mercury (THg) was strongly correlated with riparian wetland groundwater THg over the growing season. Water data analysis revealed that the riparian wetland is a net sink for THg and a net source of methyl mercury ( $CH_3Hg^+$ ) for the main tributary to Sunday Lake.

The second phase of this study investigated the fate of Hg once it reaches Sunday Lake. Mercury concentrations in water, zooplankton, and fish were analyzed to determine the trophic transfer of  $CH_3Hg^+$  in Sunday Lake. Methyl Hg concentrations in the lake were most correlated with  $CH_3Hg^+$  in the main tributary. Zooplankton  $CH_3Hg^+$  concentrations were lower than values observed in Wisconsin lakes, and differed between species. Mercury concentrations in yellow perch (*Perca flavescens*) of Sunday Lake averaged  $1.0 \pm 0.47$  ng/g THg (ww), and were higher than values observed in many remote regions. However, log bioconcentration factors (BF) were generally lower than values reported for yellow perch in other Adirondack lakes, suggesting that  $CH_3Hg^+$  in Sunday Lake is less bioavailable.

The results of this study contribute to the understanding of Hg cycling in remote forest-wetland-lake ecosystems. In addition, factors contributing to high yellow perch Hg concentrations are now better understood. These results, coupled with the findings from other parts of the whole-watershed project, have shed light on possible mechanisms of transformations and transfers of Hg in lake/watershed ecosystems.

**Sharpe, Charles -- MS in Environmental Engineering, 2004**  
***Mercury dynamics of Onondaga Lake and adjacent wetlands***

Abstract

In this study, the dynamics of mercury (Hg) were investigated in Onondaga Lake, NY and adjacent wetlands from April 2000 through December 2000. The investigation of Onondaga Lake focused on the temporal patterns of total Hg ( $Hg_T$ ) and methyl Hg (MeHg) concentrations in the water column, settling particles, and sediment. These values were utilized to create hypolimnetic mass balances for MeHg and  $Hg_T$  to assess the impact of external inputs to the fate of Hg within the water column. The adjacent wetlands were studied in an effort to characterize the temporal patterns of water pool concentrations of  $Hg_T$  and MeHg.

Total Hg concentrations in the water column of Onondaga Lake ranged from 1.4 to 17.5 ng/L, with MeHg ranging from "non-detect" to 11.9 ng/L. Peak concentrations of  $Hg_T$  and MeHg were observed below the thermocline during the stratified period (June through October). During fall mixing, there were uniformly elevated  $Hg_T$  concentrations throughout the water column, with an average concentration of 13.4 ng/L. This phenomenon was not associated with an increase in any ancillary measurement, including total suspended solids.

Based on a lake mass balance for  $Hg_T$  there was a six-fold increase between the input flux and sedimentation flux (2.24 to 12.3  $\mu\text{g}/\text{m}^2\text{-day}$ ), suggesting the presence of an additional source of particulate-bound  $Hg_T$  (resuspension or in-situ adsorption) to the water column of Onondaga Lake. Resuspension of sediments from the pelagic and littoral zones was determined to provide a minimal flux of Hg. The other possibility to account for the discrepancy in the mass balance was an ongoing external source (i.e., ground water, tributary) that was underestimated in the reported inputs. This additional input might be associated with the chlor-alkali facility that was operated along the western shore between 1946 and 1988. Loss of  $Hg_T$  occurred predominantly through sediment burial (12.8  $\mu\text{g}/\text{m}^2\text{-day}$ ). The hypolimnetic sediments were determined to be the dominant source of MeHg to the hypolimnion, with demethylation as the dominant fate of MeHg. There was minimal loss of  $Hg_T$  and MeHg through the thermocline via mixing between the layers.

Historic loading to Onondaga Lake was observed to be greatest during the operation of the chlor-alkali facility, which a peak load of approximately 10 kg/day. Subsequent to the legal action brought by the U.S. Attorney General, the loading

was to have been decreased to 0.2 kg/day by 1978 but was not fully achieved until after 1990. Concentrations of Hg have remained high in fish tissue despite the reduction in Hg loading to the lake, which indicates that there are other potential controlling factors.

The investigation of  $Hg_T$  and MeHg in the adjacent wetlands yielded no temporal patterns for any of the sites, but elevated  $Hg_T$  and MeHg concentrations in the wetland water columns (connected and unconnected) were observed. This observation may require a reevaluation of the plan to create more lake-fed wetlands as fish-breeding habitats.

### **Selvendiram, Pranesh -- MS in Environmental Engineering, 2004**

#### ***Application of PnET-BGC model to the Hubbard Brook and Sleepers River watersheds***

A biogeochemical model, PnET-BGC, was applied to Watershed 1 (W1) at the Hubbard Brook Experimental Forest, NH and Watershed 9 (W9) at Sleepers River, VT. Calcium was applied as  $CaSiO_3$  to W1 at the Hubbard Brook Experimental Forest (HBEF) to study the changes induced by calcium ( $Ca^{2+}$ ) supply in a base-poor forest ecosystem. The model was applied to simulate the efficacy and future implications of wollastonite ( $CaSiO_3$ ) treatment at W1. Different levels of emission controls on sulfur dioxide ( $SO_2$ ) and nitrogen oxide ( $NO_x$ ) and its effects on watershed treatment were evaluated. The model was also applied to W9 to evaluate the biogeochemical response and to interpret sulfur (S) isotope analysis and S dynamics at Sleepers River. Sulfur budgets of W9 at Sleepers River were compared with Watershed 6 (W6) at the HBEF.

Based on the dissolution rate of wollastonite considered in the model ( $3.5 \times 10^{-15} \text{ mol cm}^{-2} \text{ s}^{-1}$ ), nearly 90% of the applied wollastonite will be dissolved by 2010. Predicted results of watershed treatment indicate that most of the added  $CaSiO_3$  will be sequestered in soil and vegetation. The soil % base saturation will achieve the target value of 19% by the year 2004 and will reach ~25% by the year 2050. Due to treatment, the soil exchange  $Ca^{2+}$  pool reached a value of  $44 \text{ keq ha}^{-1}$  by 2050 and was higher compared to the background value in 1850 of  $31 \text{ keq ha}^{-1}$ . After the treatment soil solution molar Al/Ca ratio decreased by more than 80% relative to pretreatment values. Model simulations indicate that watershed treatment will result in the long-term increase in stream water pH and ANC of W1. Long-term simulations indicate that the applied  $Ca^{2+}$  will be an important source for plant uptake over the next ten decades. Gradual release of  $Ca^{2+}$  from soil and vegetation will provide a long-term neutralizing mechanism for surface waters at W1 and aquatic systems downstream. The benefits of watershed base treatment improved correspondingly when different levels of emission controls on S and N oxides were considered. Due to its long-term implications on biota and aquatic ecosystems, watershed base treatment can be an efficient management option compared to direct application of base material to surface waters.

Sleepers River watershed is underlain by bedrock type that is rich in S minerals and base cations. The model predicted a plant  $Ca^{2+}$  uptake rate of  $198 \text{ kg ha}^{-1} \text{ yr}^{-1}$

indicating  $\text{Ca}^{2+}$  abundance at W9. Simulated soil % base saturation was ~50%. A dry-to-wet S deposition ratio of 44%, a net weathering release of S of  $11 \text{ kg ha}^{-1} \text{ yr}^{-1}$  can explain the stream water  $\text{SO}_4^{2-}$  losses at W9 during the period 1992-2000. Sulfur isotopic simulations indicate that weathering has a major influence on stream water  $\text{SO}_4^{2-}$  at Sleepers River. The predicted sulfur isotope fractionation effect due to organic S mineralization was in the range from -0.3 to -0.5 ‰. Comparisons of S budget indicate that Sleepers River and Hubbard Brook watersheds are distinctly different ecosystems with respect to S cycling. Hubbard Brook is less influenced by internal S cycling, whereas Sleepers River is highly influenced by weathering contribution of S minerals.

**Chen, Limin -- PhD in Civil Engineering, August 2004**

***Modeling the response of terrestrial and aquatic ecosystems of Northeastern U.S. to changes in atmospheric deposition***

#### Abstract

In this study the integrated biogeochemical model (PnET-BGC) was applied to nearly 100 forest watersheds of the U.S. Environmental Protection Agency Direct/Delayed Response Program in the northeastern U.S. to investigate response of soil and surface waters in the northern forest region to effects of atmospheric deposition and changes in atmospheric deposition. Through application of the model, factors affecting spatial and temporal patterns in lake sulfate were investigated. The responses of soil and surface waters in the region to three future emission control scenarios were also evaluated. The structure of PnET-BGC was also altered by adding multiple soil layers to better simulate seasonal patterns in surface water chemistry.

The results of regional application of the model indicated that besides atmospheric sulfur deposition, landscape characteristics of elevation, vegetation type, wetland coverage and surficial geology also affect the retention of sulfate within the watersheds, influencing spatial patterns and temporal changes in lake sulfate across northern forest area of the Northeast. In response to three future emission control scenarios, soil and surface waters in the region are expected to recover from elevated atmospheric deposition, with the most aggressive control scenarios resulting in the fastest rates of recovery. Although marked recovery is expected, biologically relevant soil and surface water chemistry at regional sites are not expected to fully recover above the threshold indicator values by 2050. As a result the recovery of forest ecosystems from elevated atmospheric acidic deposition is expected to be a slow process requiring many decades to accomplish. The two-layer formulation of the model is able to mimic changes in hydrologic flow paths among different seasons and simulate stream water as a result of the mixing of soil water from the upper and lower soil layer. The two-layer model was applied at a northern forest ecosystem in New Hampshire, the Hubbard Brook Experimental Forest (HBEF), demonstrating the ability to effectively simulate seasonal variations in stream chemistry. The two soil-layer model was also used to evaluate the management options for mitigating the short-term acidification. The results indicated a full year nitrogen reduction is better in mitigating the short-term

acidification than a summer-only reduction scenario and a reduction in sulfate deposition will better mitigate the seasonal acidification than an equivalent reduction in nitrate deposition.

## **Dr. Chris Johnson's Students**

**Ussiri, David A.N. – PhD in Civil Engineering, Fall 2003**

***Organic matter chemistry and dynamics in a forest soil affected by clear-cutting disturbance.***

### Abstract

Organic matter (OM) plays an important role in governing soil properties and nutrient cycling in forest ecosystems. I investigated the chemistry of soil and dissolved organic matter (DOM) in clear-cut and undisturbed site at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire using chemical methods and solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy. On average, extractable humic substances accounted for nearly 50% of soil organic matter, with alkyl C and O-alkyl C (carbohydrate) being the dominant C fractions in soils, humic substances, and dissolved organic matter. Alkyl C ranged from 30-61% of total C, while O-alkyl C comprised 20-45% of total C. Alkyl C increased, while O-alkyl C decreased with soil depth in whole soils, humin and humic acid. Aromatic C increased with soil depth in whole soils and humin, while carbonyl C increased with depth in whole soils and fulvic acids. Fulvic acid was more acidic than humic acid. Soil from higher-elevation sites exhibited greater alkyl C and lower O-alkyl and aromatic C in the Oa horizon, suggesting a greater degree of decomposition of the organic matter in the forest floor of these conifer-rich sites. Mineral soils in conifer-rich sites contained organic matter that was more aromatic than in hardwood sites. O-alkyl C decreased from 45% to 40% after clear-cutting in the Oa horizon, while soil solutions collected from the clear-cut watershed were more aromatic than the uncut watershed. Variations in humification processes, source materials, flowpaths and in-stream processes, and transport of organic matter could account for variations in the structure and chemistry of organic matter in soils, soil solution, and streams at Hubbard Brook. The sorption behavior of organic carbon (OC) was related to the content of carboxylic functional groups in the added solution. Hydrophobic OM had greater affinity to soils than hydrophilic OM, and Bh-horizon OM exhibited greater sorption than O-horizon OM. Maximum adsorption occurred at pH 4, and decreased with either an increase or decrease in pH. The pH-dependence of OM sorption probably reflects a balance between lower charge density of carboxyl groups at low pH and lower positive charge of adsorption sites at higher pH.

**Palmer, Sheila M. – PhD in Civil Engineering, Fall 2003**

***Spatial and temporal patterns in the biogeochemistry of aluminum at the Hubbard Brook Experimental Forest, New Hampshire.***

Abstract

This study describes: i) the long-term trends in the chemistry and speciation of aluminum (Al) in soil solutions and stream waters; ii) the landscape controls on the concentration of Al species in streams; and iii) Al biogeochemistry in forest floor soils in the Hubbard Brook (HB) Valley in New Hampshire.

Long-term changes in drainage water chemistry varied with position in the landscape. In Bs soil solutions at mid- to higher elevations, declines in the sum of concentrations of strong acid anions ( $C_A$ : 2[sulfate ( $\text{SO}_4^{2-}$ )] + [chloride ( $\text{Cl}^-$ )] + [nitrate ( $\text{NO}_3^-$ )]]) and smaller declines in the sum of concentrations of base cations ( $C_B$ : 2[calcium ( $\text{Ca}^{2+}$ )] + 2[magnesium ( $\text{Mg}^{2+}$ )] + [sodium ( $\text{Na}^+$ )] + [potassium ( $\text{K}^+$ )]]) were accompanied by decreases in concentrations of inorganic monomeric Al ( $\text{Al}_i$ ) with little change in pH. These changes probably reflect the release of  $C_B$  and  $\text{Al}_i$  through exchange mechanisms in response to changing inputs of mobile acid anions.

In most streams sampled in this study, there was evidence of  $\text{Al}(\text{OH})_3$  control on Al solubility. Exceptions to this mechanism occurred at stream sites where dissolved organic carbon (DOC) concentrations were elevated. For all streams, forest floor depth and drainage area together explained much of the variation in concentrations of total monomeric Al.

There was a strong relationship between organic monomeric aluminum ( $\text{Al}_o$ ) and DOC concentrations in i) the long-term record for soil solutions and ii) stream water sampled across the HB valley. Furthermore, there was strong evidence of organic matter control on Al solubility in the forest floor. Modeling scenarios indicated that organic binding sites in the forest floor are far from saturated with Al. Furthermore, Al does not appear to limit the retention of increased Ca inputs to the forest floor, which has important implications for the remedial application of Ca to forest soils.

Despite these findings, there may be continuing stress to forest biota from elevated Al concentrations. This is particularly true at mid-to higher elevations, where Al concentrations in fine root tissues are highest and where  $\text{Ca}^{2+}/\text{Al}_i$  ratios in Bs soil solutions are persistently low (molar ratio < 1).

**Dr. Ray Letterman's Students**

**Zhang, Hao - PhD Dissertation -- In progress 2004**

**"Modeling the Removal of Humic Substances in Enhanced Coagulation"**

**Gascon, Jofelle - MS Thesis -- In progress 2004**

**"Development and Testing of a Linear Calibration Procedure for Low-Level Turbidity Measurements"**

**Anand, Gunwant Singh - MS Thesis -- December 2004**

**"Corrosion Control Using Calcium Silicate Contactors"**

**Sriram, Anant - MS Thesis -- December 2004**

**"Dissolution of Wollastonite in a Packed Bed Contactor"**

**Hsu, Hao Chen - MS Thesis -- November 2003**

**"Testing the Effect of Bubbles on On-Line and Bench Top Turbidimeters"**

**Dwarakanathan, Jamuna - MS Thesis -- June 2001**

**Testing the Agreement of On-Line Turbidimeters at Low Turbidity Levels"**

**Viswanathan, Sudhakar - MS Thesis -- July 2001**

**"Testing the Agreement of Bench Top and Portable Turbidimeters at Low Turbidity Levels"**

**Ramaswamy, Meenakshi - MS Thesis -- August 2000**

**"Count Performance Evaluation of On-Line Particle Counters",**

### **Dr. Samuel Clemence's Students**

**Farber, David -- MS in Civil Engineering, Fall 1992**

***Effect of Hydraulic Gradient and Organic Contaminants on Hydraulic Conductivity of Clay-Rich Soils***

Thesis examined the effect of Polychlorinatedbiphenyls (PCB) contaminants on the hydraulic conductivity of clay soils through constant head permeability tests. Test results indicated that low concentrations of PCB leachate had no significant effect on the hydraulic conductivity of the clay soil.

**Li, YongLang -- PhD in progress**

***Behavior of Helical Grouted Foundations in Soils***

Helical Grouted foundations are deep foundations are composed of helical anchors and a grout column constructed as the anchor is inserted into the soil. This a new foundation that is being widely used in the United States. Numerous full-scale field tests have been conducted but no theoretical model to predict the uplift and bearing capacity for these foundations has been developed. This research will include the development of a theoretical basis for predicting capacities using computer modeling and analytical models based on field data.

## **Dr. Riyad Aboutaha's Students**

### **Chutarat, Nuttawat -- PhD in Civil Engineering, Fall 2001**

#### ***Relocating Beam Plastic Hinge Regions by the Use of Headed Bars***

##### Abstract

In seismic regions, formation of a beam plastic hinge at the face of a column results in yielding of the beam reinforcing bars at the face of the column, as well as, into the beam column joint. Yielding of the reinforcing bars in the beam-column joint results in bond deterioration between the reinforcing bars and the surrounding concrete. If not well-detailed, joint deterioration may result in serious strength and stiffness degradation in the joint region.

Relocating plastic hinges in beams moves the plastic mechanism away from the column face. In practice, this has been done by bending some of the longitudinal bars at a predetermined plastic hinge location, or increasing the depth of the beam cross section at the face of the column. Both details are not very practical.

This research project involved an experimental investigation of a practical solution for relocating potential beam plastic hinge regions by the use of headed bars. Four large-scale beam-column sub-assemblages, with and without headed bars, were tested under quasi-static cyclic lateral loads/displacements. Test results of these specimens suggest that straight-headed bars are very effective in relocating beam potential plastic hinge regions.

### **Kim, SangHun -- PhD in Civil Engineering, Spring 2003**

#### ***Ductility of Carbon Fiber-Reinforced Polymer (CFRP) Strengthened Reinforced Concrete Beams***

##### Abstract

Strength of reinforced concrete beams can be easily increased by the use of externally bonded CFRP composites. However, the mode of failure of CFRP strengthened beam is usually brittle due to tension-shear failure in the concrete substrate or bond failure near the CFRP-Concrete interface. In order to improve the ductility of CFRP strengthened concrete beams, critical variables need to be investigated.

This experimental and analytical research focused on a series of reinforced concrete beams strengthened with CFRP composites to enhance the flexural capacity and ductility. The main variables were the amount of CFRP composites, the amount of longitudinal and shear reinforcement, and the effect of CFRP end diagonal anchorage system. Sixteen full-scale beams were investigated. A new design guideline was proposed reflecting the effects of the above-mentioned variables. The experimental and analytical results were found to be in good agreement.

**Wattanadechachan, Prapun -- PhD in Progress**

***Durability of Wearing Surfaces for FRP Bridge Decks***

Abstract

One attempt to lift the imposed weight limits and to solve bridge deck deterioration problems is to use fiber reinforced polymer (FRP) composite decks to replace existing deteriorated concrete bridge decks. FRP decks offer the advantages of high strength to weight ratio, ease of transport and installation, short construction time, high corrosion resistance, and high fatigue resistance.

Wearing surface material is needed on bridge decks for skid and wear resistance and to withstand the daily traffic loads during the service life of the bridge. For FRP decks, a wearing surface also serves as a cover to protect the slick and soft-top surface of the panels. Field surveys in several USA states have shown fast deterioration of wearing surface materials (WSM). The cause of deterioration is attributed to incompatibility between the WSM and the FRP decks, and several other physical and environmental factors.

This research project involved experimental investigation of several types of WSM for FRP bridge decks, e.g. polymer modified concrete, polymer concrete, asphalt, and polymer modified asphalt. In addition to material properties of individual materials, thermal compatibility between WSM and FRP was investigated using ASTM C884 Standard Test, freeze-thaw-heat non-standard test, and submerge-freeze non-standard test. A hybrid wearing surface system, which offers both excellent bond to the FRP bridge deck and excellent wearing resistance to traffic loads has been developed and recommended.

**Park, SangDon -- PhD in Progress**

***Nonlinear Strut-Tie Method Approach for FRP Strengthened Pier Cap Beams***

Abstract

Carbon fiber reinforced polymer (CFRP) composites are very effective in strengthening reinforced concrete bridge components. Over the last decade, the CFRP retrofitted systems have been investigated to produce safe and practical design regulations for structural concrete systems. The design regulations, however, fall mainly into the flexural and shear strengthening for slender beams.

As a result, in current design practice, CFRP strengthened beams can be designed with good accuracy, while CFRP strengthening of D-region is analyzed using rules-of-thumbs, common sense, and past experience.

Since bonded CFRP acts as an additional reinforcement, Strut-Tie Method also can be a powerful analysis tool for FRP retrofit system of D-region, such as deep beams or bridge pier cap beams. In addition to strut-tie model analysis, this project also involves finite element analysis of CFRP strengthened concrete bridge piers. The main objective of this research is to develop practical approach for analyzing CFRP strengthened deep structural concrete members using strut-tie method.

## **Dr. Eric Lui's Students**

**Liu, Ying – MS in Civil Engineering, 2000**

***Static and Dynamic Responses of Horizontally Curved Bridges***

### Abstract

For aesthetic consideration as well as simplicity in arrangement, details, and construction, the use of curved members has increased considerably for highway bridges located on horizontally curved alignments. This necessitates the study of the static and dynamic responses of horizontally curved bridges.

Although much work has been reported on the subject, most of the studies apply only to curved beams or girders. The study of the static and dynamic behavior of curved bridges of which curved beams (i.e., stringers) are only a part has been scanty. In particular, very little work has been done to investigate the static and free vibration response of horizontally curved bridges taking into consideration the influence of curvature, diaphragm spacing and diaphragm stiffness effects. The purpose of this study is to investigate the effect of curvature, diaphragm spacing and diaphragm stiffness on the static and dynamic responses of curved bridges.

A finite element model that can be used to represent the three main components of a bridge superstructure: the bridge deck, the supporting stringers and the diaphragms is developed for the present study. The general purpose finite element program (ANSYS5.5) is used to conduct the analyses and the parametric study. The bridges are modeled using 3-D uniaxial Beam4 elements and nonlinear multi-layer Shell91 elements in ANSYS5.5. The validity of this finite element model is established through comparison with theoretical and numerical solutions available in the literature.

A straight bridge and three horizontally curved bridges with three different values of diaphragm stiffness and diaphragm spacing are considered. Only service gravity loadings that consist of the dead weight of the bridge and the AASHTO HS25 truck load and lane load are used in the study.

The results show that the effect of curvature is more pronounced than diaphragm stiffness and diaphragm spacing in influencing the dynamic response of curved bridges. Nevertheless, the effect of diaphragm spacing becomes more important for curved bridges, especially when torsion dominated modes are involved.

**Wang, Jian – MS in Civil Engineering, 2003**

***The effects of lightweight backfill on the dynamic behavior of highway bridges with integral abutments***

Abstract

Lightweight materials (e.g., tire chips, geof foam, lightweight sand) are often used as backfill to reduce lateral pressure on structural foundations and retaining walls. These materials have also been used as backfill for integral abutment bridges. Because the analysis and design of integral abutment bridges should take into consideration the effect of soil-structure interaction, it is conceivable that the properties of the backfill material will have an influence on the behavior of the bridges. Thus far, most of the studies reported in the literature addressed only the static aspect of this problem, the effects of these materials on the dynamic behavior of bridges have not been systematically studied.

In this study, a simple integral abutment bridge model is analyzed using dynamic theories. Based on the results of this simple model, more realistic 2-D and 3-D soil-structure interaction models that include the bridge structure, backfill and soil are built using the finite element method (FEM). Harmonic seismic excitation and spectral analyses are applied to these 2-D and 3-D models to conduct parametric studies to investigate the effects of the various combinations of backfill mass density, backfill elastic modulus and system damping ratio on the dynamic response of the bridge. The harmonic excitation and spectral analysis results from the 2-D and 3-D models are compared and conclusions are drawn based on these analysis results.

The results show that the effects of damping and elastic modulus of the backfill material are more important than the backfill mass density in influencing bridge responses. The dynamic responses (e.g., moment, displacement) of integral abutment bridges decrease when a material with high damping and elastic modulus is used as backfill.

**Meng, Junyi, PhD in Civil Engineering, 2000**

***Seismic analysis and evaluation of skew highway bridges***

Abstract

A theoretical and experimental investigation of the seismic response of skew highway bridges is presented. The study begins with the description of a rigid deck bridge model for short span skew bridges. Formulas for computing earthquake response are developed, and parameters that significantly influence

the dynamic response of the bridges are identified. The study indicates that the response of a given skew bridge depends not only on its deck aspect ratio, the stiffness eccentricity ratio, the skew angles, and its natural frequencies, but also on its frequency ratio.

For longer span skew bridges, the use of the rigid deck assumption is questionable. To study the effect of deck flexibility, finite element models are developed to study the behavior of a representative medium span skew reinforced concrete box girder bridge. The effects of superstructure flexibility, substructure boundary conditions, structural skewness and stiffness eccentricity on the seismic response of the bridge are studied using response spectrum analyses.

A refined stick model that utilizes a dual-beam representation of the bridge deck is proposed for preliminary dynamic analysis and seismic assessment of medium or long span skew bridges. The validity of the model is established by comparing results with numerical solutions obtained for skew plates and a skew bridge.

When bridges are subjected to moderate-to-strong earthquakes, inelasticity often occurs at incipient failure. The nonlinear analysis of skew highway bridges is performed using nonlinear time history analysis procedure and the AASHTO design approach. Through comparison of the two approaches, the deficiency of the current AASHTO approach is identified.

During an earthquake, both horizontal and vertical ground motions are imparted to the bridge structure. The effects of both these earthquake components are studied. The results show that the vertical earthquake component affects the column axial force noticeably, but its effect on shear and moment is only secondary.

To validate the theoretical and numerical analyses, an experimental study on a model skew bridge is carried out. Tests for static displacements, natural frequencies, mode shapes and damping of the model bridge are conducted. Good correlation is obtained for the theoretical and experimental results.

**Oguzmert, Metin – PhD in Progress**

***A Comprehensive Method for Performance Based Earthquake Design of Buildings***

**Ge, Ma – PhD in Progress**

***Structural Damage Detection and Identification Using System Dynamic Parameters***